# PATENT SPECIFICATION

Application Date: Dec. 3, 1941. No. 15567/41. **553,004**

Complete Specification Left: Dec. 1, 1942.

Complete Specification Accepted: May 4, 1943.

PROVISIONAL SPECIFICATION

## Process and Apparatus for Regenerating Exhaled Air

I, NICOLAS HERZMARK, of Airsealand Limited, 43, London Wall, London, E.C.2, a Citizen of France, do hereby declare the nature of this invention to be as follows:—

This invention relates to the regeneration of exhaled air, for example in confined spaces, such as the interior of submarines, and in respirators for fire-fighting and life-saving equipment.

Air-regeneration requires an addition of oxygen to replace that absorbed in the lungs and a fixation of the exhaled carbon dioxide, so as to maintain the proportions within suitable limits, viz. not less than 12 percent of oxygen and not more than 8 percent of carbon dioxide.

The carbon dioxide can be neutralized by alkali hydrates or oxides, with which it forms carbonates; for the supply of oxygen, there is commonly employed either oxygen under pressure or oxygen provided by alkali peroxides under the action of water vapour. These methods are subject to serious disadvantages, since the employment of compressed oxygen requires containers such as steel bottles, which are heavy and costly; on the other hand, the alkali peroxides are sensitive to the action of moisture alone, so that they give off oxygen when exposed to humidity of any kind, irrespective of the presence of carbon dioxide. Moreover, the peroxide granules humidified and carbonated by the passage of moist air containing carbon dioxide become covered with a film of carbonate which masks the centre of the granule from further reaction, and they may become agglomerated into blocks which stop the penetration of air into the mass.

The present invention comprises an improved regeneration process employing as a source of oxygen a mixture of peroxides or per-salts with one or more substances insensitive to the action of moisture alone but converted by carbon dioxide into another body which will determine (by catalysis or otherwise) the evolution of oxygen from the mixture in presence of moisture; suitable substances for this purpose are the insoluble alkaline-earth metal manganates (such as barium manganate) which are converted by weak acids (such as carbon dioxide) into soluble permanganates, the latter reacting with suitable proportions of the alkali peroxides or per-salts in the mixture to produce free oxygen as follows:—

$$4\,Na_2O_2 + Ba(MnO_4)_2 + 5\,H_2O = 8\,NaOH + Mn_2O_3 + Ba(OH)_2 + 8\,O.$$

If the manganates are in smaller proportions, the permanganates formed by the action of carbon dioxide will act as catalysts to assist the evolution of oxygen.

In addition to the fixation of carbon dioxide by the decomposition of the manganates to form permanganates, a further quantity may be absorbed by means of alkaline-earth metal ferrates, which are very stable in the absence of acids but have a great affinity for carbon dioxide; these ferrates are very active carbonating catalysts. In mixture with the peroxides or per-salts and alkaline-earth metal manganates, they form products very sensitive to the action of exhaled air containing carbon dioxide; porous or fibrous materials, such as asbestos, can be added to the mixture, over which the air can be passed either by natural ventilation or under pressure from fans.

By way of example, and without being limited thereto, the following mixtures may be employed:—

| | | |
|---|---|---|
| A. | Sodium perborate - - | 80 parts |
| | Barium manganate - | 10 ,, |
| | Asbestos - - - - - - | 10 ,, |
| B. | Barium dioxide - - | 25 parts |
| | Barium ferrate - - | 5 ,, |
| | Sodium peroxide - - | 50 ,, |
| | Barium manganate - | 10 ,, |
| | Asbestos - - - - - - | 10 ,, |

The mixture (A) having a base of perborate will be particularly stable in the absence of carbon dioxide; under the combined action of the latter and moisture, the mixture will liberate its oxygen whilst neutralizing relatively little carbon dioxide. The mixture (B) having a base of peroxide will liberate oxygen and will also neutralize a large proportion of carbon dioxide. In practice, the two mixtures will preferably be used in

conjunction.

These mixtures will be composed of ordinary commercial substances, in fine powder form, and short fibres of asbestos (some millimetres in length), intimately mixed by the aid of known commercial mixers (kneading type), in a dry atmosphere containing very little carbon dioxide. The mixtures can be compressed at 15 to 20 kg. per sq. cm. between metallic wire gauzes, the frames so formed being either suspended in the confined space or arranged in the passage or outlet for exhaled air or in a pipe or box through which the air is blown. The frames can be enclosed before use in sealed metal boxes, sheltered from humidity and from the atmosphere. At the time of use, they can be hung up or arranged in convenient positions to any desired number. Proportionately as they become exhausted, they will be replaced by new ones. But it will be noted that by moistening them, at the end of normal service, there will be obtained a fresh liberation of oxygen and a fresh absorption of carbon dioxide.

Besides the regenerative results described, the improved process presents other characteristics:—

(a) Acid vapours are neutralized, liberating oxygen.

(b) Hydrogen, coming for example from an accumulator battery, is transformed into water which reacts, as stated, to liberate oxygen.

(c) Organic respiratory products are oxidized.

It will thus be seen that the present invention is of particular importance for regenerating air in confined spaces where the content of oxygen has become diminished and human life has thereby become endangered.

Dated this 3rd day of December, 1941.

For the Applicant,
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COMPLETE SPECIFICATION

## Process and Apparatus for Regenerating Exhaled Air

I, NICOLAS HERZMARK, of Airsealand Limited, 43, London Wall, London. E.C.2, a Citizen of France, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the regeneration of exhaled air, for example in confined spaces, such as the interior of submarines, and in respirators for fire-fighting and life-saving equipment.

Air-regeneration requires an addition of oxygen to replace that absorbed in the lungs and a fixation of the exhaled carbon dioxide, so as to maintain the proportions within suitable limits, viz. not less than 12 percent of oxygen and not more than 8 percent of carbon dioxide; beyond these limits, the atmosphere will not support human life without distress and for persons working in a closed space having such an atmosphere it is necessary to provide air regeneration, which entails the supply of oxygen and the elimination or neutralization of the carbon dioxide by chemical reaction. According to Paul Bert, a man performing moderate work absorbs every hour about 22 litres of oxygen and exhales about 18 litres of carbon dioxide with 35 grammes of water vapour. The tolerance of the human organism is fairly great, since satisfactory respiration can be maintained if the proportion of carbon dioxide does not exceed 9 percent and if the quantity of oxygen available is at least 10 percent.

The carbon dioxide can be neutralized by alkali hydrates or oxides, with which it forms carbonates; for the supply of oxygen, there is commonly employed either oxygen under pressure or oxygen provided by alkali peroxides under the action of water vapour. These methods are subject to serious disadvantages, since the employment of compressed oxygen requires containers such as steel bottles, which are heavy and costly; on the other hand, the alkali peroxides are sensitive to the action of moisture alone, so that they give off oxgyen when exposed to humidity of any kind, irrespective of the presence of carbon dioxide. Moreover, the peroxide granules humidified and carbonated by the passage of moist air containing carbon dioxide become covered with a film of carbonate which masks the centre of the granule from further reaction, and they may become agglomerated into blocks which stop the penetration of air into the mass.

It has also been proposed to regenerate impure air for respiration by bringing an easily deoxidisable liquid (for example, hydrogen peroxide) into contact with a catalyst (potassium permanganate being mentioned as suitable) in predetermined amounts, the oxygen developed thereby being introduced into a tube or channel conveying the exhaled air, and said tube or channel being provided with one or

more cartridges for absorbing carbon dioxide from the air before, after or both before and after the introduction of oxygen evolved by the catalytic action.

The present invention comprises an improved process for regeneration of exhaled air by subjecting it to regenerating agents and carbon-dioxide neutralizing agents, employing as a source of oxygen a stable mixture of peroxides or per-salts with one or more substances insensitive to the action of moisture alone but converted by carbon dioxide into another substance which will cause (by catalysis or otherwise) the evolution of oxygen from the mixture in presence of moisture; suitable substances for this purpose are the insoluble alkaline-earth metal manganates (such as barium manganate) which are converted by weak acids (such as carbon dioxide) into soluble permanganates, the latter reacting with suitable proportions of the alkali or alkaline-earth metal peroxides or per-salts in the mixture to produce free oxygen by a coupled reaction of the type:—

$$4\,Na_2O_2 + Ba(MnO_4)_2 + 5\,H_2O = 8\,NaOH + Mn_2O_3 + Ba(OH)_2 + 8\,O.$$

If the manganates are in smaller proportions than necessary for conversion into permanganates for complete reaction with the peroxides or per-salts, the permanganates formed by the action of carbon dioxide will act as catalysts to assist the evolution of oxygen from the peroxides or per-salts.

In addition to the fixation of carbon dioxide by the decomposition of the manganates to form permanganates, and by combination with the alkali or alkaline-earth hydroxides to form carbonates, a further quantity may be absorbed by means of alkaline-earth metal ferrates; these ferrates, which are very stable in the absence of acids but have a great affinity for carbon dioxide, are very active carbon-dioxide neutralizing agents. In mixture with the peroxides or per-salts and alkaline-earth metal manganates, they form products very sensitive to the action of exhaled air containing carbon dioxide; porous or fibrous materials, such as asbestos, can be added to the mixture, over which the air can be passed either by natural ventilation or under pressure from fans.

By way of example, and without being limited thereto, the following mixtures may be employed:—

| | | |
|---|---|---|
| A. | Sodium perborate - - | 80 parts |
| | Barium manganate - | 10 ,, |
| | Asbestos - - - - - | 10 ,, |
| B. | Barium dioxide - - | 25 parts |
| | Barium ferrate - - | 5 ,, |
| | Sodium peroxide - - | 50 ,, |
| | Barium manganate - | 10 ,, |
| | Asbestos - - - - - | 10 ,, |

The mixture (A) having a base of perborate will be particularly stable in the absence of carbon dioxide; under the combined action of the latter and moisture, the mixture will liberate its oxygen whilst neutralizing relatively little carbon dioxide. The mixture (B) having a base of peroxide, and likewise stable in the absence of carbon dioxide, will liberate oxygen and will also neutralize a large proportion of carbon dioxide when exposed thereto. In practice, the two mixtures will preferably be used in conjunction.

These mixtures will be composed of the ordinary commercial substances, in fine powder form, and short fibres of asbestos (some millimetres in length), intimately mixed by the aid of known commercial mixers (kneading type), in a dry atmosphere containing very little carbon dioxide. The mixtures can be compressed at 15 to 20 kg. per sq. cm. between metallic wire gauzes, the frames so formed being either suspended in the atmosphere of the confined space or arranged in the passage or outlet for exhaled air or in a pipe or box through which the air is blown. The frames can be enclosed before use in sealed metal boxes, sheltered from humidity and from the atmosphere. At the time of use, they can be hung up or arranged in convenient positions to any desired number. Proportionately as they become exhausted, they will be replaced by new ones. But it will be noted that by moistening them, at the end of normal service, there will be obtained a fresh liberation of oxygen and a fresh absorption of carbon dioxide.

The commingling of the material with the short asbestos fibres results in a dissemination of the material and the subjection to the action of the atmosphere in the closed space of maximum regenerating and purifying surfaces and the maximum and continuous chemical reaction and at the same time prevents the material from accumulating in a solid mass and forming agglomerates and producing undesirable heat which have rendered other processes objectionable.

Tests of the process demonstrate that there is a neutralization of carbon dioxide with the simultaneous production of oxygen which permits long-continued respiration in an enclosed space.

In carrying out the tests a test cabin of iron sheeting having a capacity of 1300 litres was employed. The testing

room of the cabin, which was provided with an air-tight door in addition to a manometer was equipped with a thermometer and valves for controlling the introduction and escape of gas through tubular connections, and an interior ventilating fan was provided.

Two frames, one supporting the material (B) neutralizing carbon dioxide and partially generating oxygen, and the other supporting the material (A) almost solely generating oxygen, and containing a total of 4.4 kgs. of compressed active matter, were suspended in the cabin. On a table adjacent to the cabin was placed an apparatus of well known type for supplying carbon dioxide to the closed space of the test cabin. The delivery tube passed the gas through a glass water container calibrated by means of two lines, the space between which corresponded to 70 cu. cms. An Orsat apparatus was provided for the analysis and measurement of the gases discharged from the cabin.

Batches weighing 141 grams each of bicarbonate of soda were prepared for use in the $CO_2$ apparatus, each representing the necessary quantity to emit, upon the addition of 55 cu. cm. of sulphuric acid diluted to 66% in water, a volume of carbon dioxide equal to 37 litres.

It was found that approximately one litre of gas remained in the container and piping at each test, showing that 36 litres were introduced in the cabin. This quantity of carbon dioxide is equivalent to that exhaled during two hours by one man (according to Paul Bert). In the same time, the man's breath will exhale about 70 grams of water vapour.

At 10-30 a.m., the cabin was closed. The thermometer reading was 22° C. 36 litres of carbon dioxide were introduced while the air was agitated at intervals by means of the fan. At 11-15 a.m., the operation was terminated. The manometer showed a pressure of 48 cm. The pressure was released until a pressure of 2 cm. was shown, the air ejected being tested in the Orsat apparatus. The pressure drop of 46 cm. indicated that 60 litres had been removed from the cabin, which 60 litres contained

| | |
|---|---|
| $CO_2$ - - - | 1.2% |
| O - - | 21.4% |

At 11-25 a.m., the interior temperature was 23° C. A further dose of 36 litres of carbon dioxide and 70 grams of water vapour was introduced into the cabin.

At 12-35 p.m., the pressure was 41 cm., which was let down to 2 cm. and analysis of the escaping air was carried out. 50 litres of air were discharged, containing:

| | |
|---|---|
| $CO_2$ - - | 1.2% |
| O - - | 23.2% |

At 12-30 p.m., the temperature was 25° C. Again, 36 litres of carbon dioxide and 70 grams of water vapour were introduced into the cabin and the operation was stopped at 1-20 p.m. The pressure of 63 cm. was reduced to 4 cm., indicating that 77 litres of air had been removed, containing:

| | |
|---|---|
| $CO_2$ - - | 1.8% |
| O - - | 27.4% |

At 1-40 p.m., once more 36 litres of carbon dioxide and 50 grams of water vapour were introduced into the cabin. Operation was stopped at 2-5 p.m. with the pressure standing at 65 cm., which was reduced to 60 cm., that is to say 78 litres of air were removed, containing:

| | |
|---|---|
| $CO_2$ - - | 3.2% |
| O - - | 30.6% |

The cabin was left, without any addition of gas or ventilation of the contents until 3-30 p.m.; it was then found that the pressure had dropped to a partial vacuum of 10 cm. The temperature reading was 24° C.

At 3-30 p.m., 36 litres of carbon dioxide and 70 grams of water vapour were introduced into the cabin. Testing showed:

| | |
|---|---|
| $CO_2$ - - | 3.2% |
| O - - | 31.7% |

The cabin was left without addition of carbon dioxide until 5-15 p.m. The pressure reading was then 6 cm. Testing showed:

| | |
|---|---|
| $CO_2$ - - | 2.4% |
| O - - | 32. % |

Between 5-15 and 5-45 p.m., 36 litres of carbon dioxide and 60 grams of water vapour were introduced, and at 6-0 p.m. the pressure was 31 cm. Testing showed:

| | |
|---|---|
| $CO_2$ - - | 4.2% |
| O - - | 32.2% |

The cabin was left without ventilation until the following day and in the morning at 8-45 a.m., there was a partial vacuum of 6 cm. The temperature was 18° C. Testing of the contents showed:

| | |
|---|---|
| $CO_2$ - - | 0.3% |
| O - - | 34.1% |

At 5-15 p.m., that is to say, six hours and forty-five minutes after starting the experiment, with a stop of one hour, the calculation of the oxygen yield and of the neutralized carbon dioxide was made up as follows:—

OXYGEN.

At the beginning of the experiment, the cabin contained 1300 litres of air with 20.8% of oxygen, i.e. - - - - - - - - - - 270 litres

At 5-15 p.m., the pressure was 6 cm. The difference in temperature was 3°. The temperature correction gives 11.4 cm. the true difference of pressure being therefore 5.4 cm. or 7 litres. This makes (1300 – 7 =) 1,293 litres with 32% of oxygen equal to: 413 litres

There have been discharged successively: —

| | | | litres | |
|---|---|---|---|---|
| At 11-15 a.m., | 60 litres containing | 21.4% - - - - | 12.8 | |
| ,, 12-25 p.m., | 50 ,, ,, | 23.2% - - - - | 11.6 | |
| ,, 1-20 p.m., | 77 ,, ,, | 27.4% - - - - | 21.1 | |
| ,, 2- 5 p.m., | 78 ,, ,, | 30.6% - - - - | 23.8 | |
| | | Total - - - | | 69.3 ,, |
| | | Grand total - - | | 482.3 ,, |
| Net amount of oxygen generated - - - - | | | | 212 ,, |

CARBONIC ACID.

Up to 5-15 p.m. there have been introduced 5 times 36 litres, i.e. 180 litres

| | | | litres | |
|---|---|---|---|---|
| There have been discharged | 60 litres at | 1.2% - - - | 0.7 | |
| | 50 ,, ,, | 1.2% - - - | 0.6 | |
| | 77 ,, ,, | 1.8% - - - | 1.2 | |
| | 78 ,, ,, | 3.2% - - - | 2.5 | |
| There remain 1,293 litres at | | 2.4% - - - | 31. | |
| | | Total - - - | | 36 |
| Amount neutralized - - - - - - - - | | | | 144 litres |

After 15 hours of rest: —

OXYGEN.

Amount at the start of the experiment - - - - - 270 litres
At the end of the experiment, depression 6 cm., difference of temperature 4° C., representing 15 cm. True difference of pressure 21 cm. or 27 litres. This makes (1300 – 27 =) 1,273 litres, with 34.1% of oxygen, equal to - - - - - - - - 433 litres
There have been discharged - - - - - - 69 litres

| | | |
|---|---|---|
| Total - - - | | 503 litres |
| Net amount of oxygen generated - - - - - - | | 233 litres |
| Carbon dioxide has been introduced 6 times, 36 litres each time, i.e. | | 216 litres |
| There have been discharged - - - - - - | 5 litres | |
| There remain 1,273 litres of air with 0.3 % $CO_2$, i.e. - | 4 ,, | |
| Total - - - | | 9 litres |
| Amount neutralized - - - - - - - - | | 207 litres |

From the foregoing it will be clear that there was a neutralization of carbon dioxide simultaneously with the production of oxygen, which enables exhaled air to be purified and regenerated.

The liberation of 212 litres of oxygen corresponds to a consumption of approximately ten man-hours; that of 233 litres

corresponds to eleven man-hours. The neutralization of 144 litres of carbon dioxide corresponds to the production of carbon dioxide exhaled by one man during eight hours and that of 207 litres corresponds to his exhalation during eleven and one-half hours.

On the assumption that the exhaustion of the product is to occur at twenty hours from the starting of the test, and allowing for the purifying and regeneration of exhalation for eleven man-hours, it is evident that the amount of material required per hour for breathing is 0.400 kg. per man.

Besides the regenerative results described, the improved process presents other characteristics:—

(a) Acid vapours are neutralized, liberating oxygen.

(b) Hydrogen, coming for example from an accumulator battery, is transformed into water which reacts, as stated, to liberate oxygen.

(c) Organic respiratory products are oxidized.

It will thus be seen that the present invention is of particular importance for regenerating air in confined spaces where the content of oxygen has become diminished and human life has thereby become endangered.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. An improved process for regeneration of exhaled air, by subjecting it to oxygenating agents and carbon-dioxide neutralizing agents, employing as a source of oxygen a stable mixture of one or more peroxides or per-salts with one or more substances insensitive to the action of moisture alone but converted by carbon dioxide into another substance which will cause the evolution of oxygen from the mixture in presence of moisture.

2. A process according to claim 1, in which the exhaled air is subjected to the action of a mixture of an oxygen-yielding substance consisting of an alkali or alkaline-earth metal peroxide or per-salt, and an insoluble manganate transformable by carbon dioxide into a soluble permanganate which will yield oxygen simultaneously with the absorption of carbon dioxide.

3. A process according to claim 1 or 2, in which the mixture includes an insoluble manganate consisting of an alkaline-earth manganate.

4. A process according to any of the preceding claims, in which the mixture includes one or more alkaline-earth metal ferrates.

5. A process according to claim 3, in which the mixture is composed mainly of sodium perborate with barium manganate and a porous or fibrous material, approximately in the proportions stated in Example A.

6. A process according to claims 3 and 4, in which the mixture is composed mainly of one or more alkali or alkaline-earth metal peroxides with an insoluble alkaline-earth metal manganate, an alkaline-earth metal ferrate, and a porous or fibrous material.

7. A process according to claim 6, in which the mixture is composed mainly of sodium peroxide and barium dioxide, with barium manganate, barium ferrate and a porous or fibrous material, approximately in the proportions stated in Example B.

8. A process according to claim 1, 2 or 3, in which two mixtures are used in conjunction, one being as defined in claim 5 and the other as defined in claim 6.

9. Apparatus for regenerating exhaled air, comprising a frame or frames formed of metallic wire gauzes, adapted for suspension in the atmosphere to be regenerated or for arranging in a passage for the exhaled air, and having mounted between the gauzes, in compressed condition, a mixture or mixtures as defined in any of the preceding claims.

Dated this 1st day of December, 1942.

For the Applicant,
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15, Dominion Street, London, E.C.2.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1943